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AN APPROACH TO THE ANALYSIS OF VIBRATIONAL-ROTATIONAL INTERACTIONS IN MOLECULES

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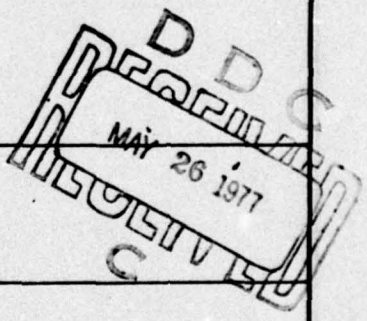

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The vibration-rotation interaction of diatomic molecules with high angular moments have been completely re-examined using a nonperturbative scheme which avoids the usual anharmonic oscillator interpretation. A second section is devoted to the evaluation of the mass-dependent contribution to the potential energy in the Watson version of the vibration-rotation Hamiltonian in terms of the generalized Lucas polynomials. The third section of the report discusses an attempt to employ Chebyschev operator expansions to the Van Vleck transformation.

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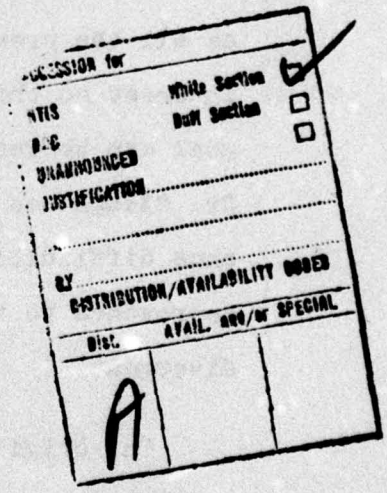

INTRODUCTION

Vibrational-rotational interactions in polyatomic (particularly diatomic and triatomic) molecules have been studied by physicists almost since the inception of quantum mechanics. The subject is extremely involved and it cannot be said that completely satisfactory solutions exist except for small amplitude situations where perturbation theoretic methods have been employed. Crucial to the perturbation approach is the van Vleck transformation whereby the solution is built up using as the zero order approximation, the Hamiltonians of the rigid asymmetric rotor and the harmonic oscillator. The conceptual simplicity of the perturbation approach is more than offset by the fact that for many molecules (e.g., H_2O) higher approximations become necessary. This places a severe burden on the computational aspects in that each higher perturbation order generally requires as much effort as all the previous orders. Now reasonably high J numbers are of interest so that one hopes that with enough perserverence the goal can be reached by brute force calculations. However, as Dr. Clough has pointed out to the author of this report, convergence difficulties inevitably enter and in fact some perturbation approaches to the vibrational-rotational problem tend to become divergent.

The original intent was to circumvent these divergencies by applications of new analytical techniques such as matrix Padé

approximants, etc. A very considerable effort was expended toward this end. The growing realization that none of these sophisticated mathematical tricks could unlock the solution finally lead the author to seek a new representation, *ab initio*. Furthermore, it was felt that the proper test ground should be the diatomic molecule rather than the triatomic molecule. To this end, the problem of the vibrational-rotational interaction in a diatomic molecule with high angular momentum has been completely re-examined using a nonperturbative scheme which completely avoid the usual anharmonic oscillator interpretation and its attendant difficulties. This material is outlined in Section One.

Section Two is devoted to the evaluation of the mass-dependent contribution to the potential energy in the Watson molecular vibration-rotation Hamiltonian. An explicit solution is obtained via generalized Lucas polynomials and has been checked against the solution obtained by Rothman and Clough. An abortive attempt to employ Chebyschev operator expansions to the van Vleck transformation is discussed in Section Three.

1. VIBRATION-ROTATION INTERACTION IN DIATOMIC MOLECULES WITH REFERENCE TO LARGE J VALUES

Schroedinger's equation for the vibration-rotation interaction of a diatomic molecule is

$$-X'' + [\Delta(1+q)^{-2} + V(q)]X = \Lambda X \tag{1.1}$$

where $\Delta \equiv J(J+1)$ and $X(q) \equiv q\psi(q)$.

The conventional approach by Dunham [1] is via perturbation theory. Both $V(q)$ and $(1+q)^{-2}$ are expanded in a power series in q. It is possible to eliminate the constant and the linear term in q, so that Eq. 1.1 can be expressed as

$$-X'' + (aq^2 + bq^3 + cq^4 + \cdots)X = \Lambda X \tag{1.2}$$

which is the equation of the anharmonic oscillator. The argument behind the perturbation approach is certainly plausible, one expects the terms bq^3, cq^4, $\cdots$ to be small compared to aq^2. Explicit expressions for the energy levels have been worked out in an elegant manner by Kilpatrick [2]. However, these perturbation expansions are not convergent!

In order to see this without undue complications, let us confine ourselves to the case

$$-X'' + (q^2 + cq^4)X = \Lambda X \ . \tag{1.3}$$

Straightforward application of the Rayleigh-Schroedinger

perturbation technique yields

$$\Lambda = 1 + \frac{3}{4}\, c - \frac{21}{16}\, c^2 + \frac{333}{64}\, c^3 - \cdots \qquad (1.4)$$

for the ground state energy. The coefficients do not decrease in magnitude and, in fact, the series does not converge for any nonzero value of c. Failure of the series to converge follows from the fact that a nonzero radius of convergence would have to include negative values of c (*but*, for negative c, the potential energy does not possess a lower bound as $c \to -\infty$). The spectrum, consequently, is a continuum and cannot connect continuously with the discrete spectrum for positive c. The series, Eq. 1.4, is asymptotically valid as $c \to 0$. In view of these remarks, we seek a non-perturbative solution.

An obvious approach is to expand the wave function in a linear combination of harmonic oscillator wave functions; Chan and Stelman [*3*], Reid [*4*]. However (in part preparation for our new approach), we will assume that

$$X(q) = e^{-q^2/2} \sum_{n=0}^{\infty} A_n\, q^{2n} \qquad (1.5)$$

for the even parity states and

$$X(q) = e^{-q^2/2} \sum_{n=0}^{\infty} B_n q^{2n+1} \tag{1.6}$$

for the odd parity states.

Direct substitution of these series into Eq. 1.3 yields the recurrence relations

$$cA_{n-2} - A_{n-1} + (1+4n-\Lambda)A_n - 2n(2n-1)A_{n+1} = 0 \tag{1.7}$$

$$cB_{n-2} - B_{n-1} + (3+4n-\Lambda)B_n - 2n(2n+1)B_{n+1} = 0 \tag{1.8}$$

with A_k, B_k set equal to zero if k is a negative integer. Both recurrence relations are four-fold and the eigenvalue problem is the condition that a nontrivial solution for the $\{A_n\}$, $\{B_n\}$ exist. This leads to the requirement that the Λ must be found which cause the vanishing of the infinite determinants $\hat{M}_o$ and $\hat{M}_e$ of which the 5 × 5 finite sections are:

SEE SEPARATE SHEET (1.9)

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and

SEE SEPARATE SHEET (1.10)

$$\hat{M}_e = \begin{vmatrix} 1-\Lambda & -2 & 0 & 0 & 0 \\ -1 & 5-\Lambda & -12 & 0 & 0 \\ c & -1 & 9-\Lambda & -30 & 0 \\ 0 & c & -1 & 13-\Lambda & -56 \\ 0 & 0 & c & -1 & 17-\Lambda \end{vmatrix}$$

(1.9)

$$\hat{M}_o = \begin{vmatrix} 3-\Lambda & -6 & 0 & 0 & 0 \\ -1 & 7-\Lambda & -20 & 0 & 0 \\ c & -1 & 11-\Lambda & -42 & 0 \\ 0 & c & -1 & 15-\Lambda & -72 \\ 0 & 0 & c & -1 & 19-\Lambda \end{vmatrix}$$

(1.10)

The determinants are banded and only of width four which is an obvious factor in our favor. The determinant is not symmetric, but this is not a serious problem since there are a number of packaged algorithms to evaluate eigenvalues of nonsymmetric determinants. In order to test the effectiveness of the approach, the first four even and the first four odd eigenvalues were calculated via 12 × 12 finite sections of the corresponding infinite determinants. Although no serious attempt was made to obtain very high accuracy, the results listed in Table 1.1 are in reasonable agreement with the now standard results of Reid [4] based on an harmonic oscillator basis set of one hundred.

There is no great difficulty in adding additional higher order terms to the potential, the main effect is to make the band of the eigenvalue determinant larger. Consequently if one persists in employing the anharmonic oscillator interpretation, then this nonperturbative approach is definitely useful. The main difficulty, however, is buried in the coefficients of the effective potential since $a,b,c,\cdots$ are functions of Δ. Consequently, large values of Δ (which is, after all, the real case of interest) mean that more and more coefficients of the effective potential must be included. This in turn means that the banded matrix becomes wider and computational difficulties in evaluating the eigenvalues arise because all the banded elements are in turn numerically large.

TABLE 1.1. ENERGY LEVELS OF THE QUARTIC OSCILLATOR. I, LEVELS AS COMPUTED BY REID; II, LEVELS AS COMPUTED BY PRESENT METHOD.

n	I	II
0	1.06036209048	1.060362
1	3.79967302980	3.799673
2	7.45569793799	7.455698
3	11.6447455114	11.64474
4	16.2618260189	16.26183
5	21.2383729182	21.23837
6	26.5284711837	26.52848
7	32.0985977110	32.09860
8	37.9230010270	37.92300

For this reason, we feel it is expedient to abandon the anharmonic oscillator interpretation and seek some other representation which is more natural to the intrinsic problem.

Let us return to Eq. 1.1, rewrite it in the form

$$-(1+q)^2X'' + [\Delta + (1+q)^2V(q)]X = \Lambda(1+q)^2X \qquad (1.11)$$

and deal with it directly. We feel it is more convenient and instructive to study Eq. 1.1 *ab initio* in the form Eq. 1.11 than appeal to the anharmonic oscillator interpretation. Our main interest is in large values of Δ. To this end we take as our prototype equation

$$-(1+q)^2X'' + [\Delta + (1+q)^2(bq^2+cq^3+dq^4)]X = \Lambda(1+q)^2X \ . \qquad (1.12)$$

In order to solve Eq. 1.12, assume that

$$X(q) = e^{-q^2/2}\sum_{n=0}^{\infty} C_n q^n \qquad (1.13)$$

where the C_n are as yet unknown. Unlike the previous case of the pure quartic oscillator, the expansion must include both odd and even powers of q. Upon substituting the series into Eq. 1.12, we find (after some tedious manipulations) that the C_n obey the recurrence relation

$$-(\ell+1)(\ell+2)C_{\ell+2} - 2\ell(\ell+1)C_{\ell+1} + (-\ell^2+3\ell+2+\Delta-\Lambda)C_\ell$$

$$+(4\ell-2-2\Lambda)C_{\ell-1} + (2\ell-4+\alpha-\Lambda)C_{\ell-2} + (\beta-2)C_{\ell-3}$$

$$+(\gamma-1)C_{\ell-4} + \delta C_{\ell-5} + \varepsilon C_{\ell-6} = 0 \qquad (1.14)$$

where $C_{-k} \equiv 0$ for $k = 1,2,\cdots$. Note that

$$\alpha \equiv b \quad , \quad \gamma \equiv b+2c+d \quad , \quad \varepsilon \equiv d$$

$$\beta \equiv 2b+c \quad , \quad \delta \equiv c+2d \quad . \qquad (1.15)$$

This is a nine term recurrence relation.

The eigenvalue conditions are

$$(\hat{M} - \Lambda\hat{N})\hat{C} = 0 \qquad (1.16)$$

where $\hat{C}$ is the column matrix of the as yet unknown C_n. The matrices $\hat{M}$ and $\hat{N}$ are infinite matrices. The 10 × 10 finite section of $\hat{M}$ is given by

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SEE SEPARATE SHEET (1.17)

---

while the 7 × 7 finite section of $\hat{N}$ is

SEE SEPARATE SHEET (1.18)

$$\hat{M} = \begin{vmatrix}
2+\Delta & 0 & -2 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
2 & 4+\Delta & -4 & -6 & 0 & 0 & 0 & 0 & 0 & 0 \\
\alpha & 6 & 4+\Delta & -12 & -12 & 0 & 0 & 0 & 0 & 0 \\
\beta-2 & \alpha+2 & 10 & 2+\Delta & -24 & -20 & 0 & 0 & 0 & 0 \\
\gamma-1 & \beta-2 & \alpha+4 & 14 & -2+\Delta & -40 & -30 & 0 & 0 & 0 \\
\delta & \gamma-1 & \beta-2 & \alpha+6 & 18 & -8+\Delta & -60 & -42 & 0 & 0 \\
\varepsilon & \delta & \gamma-1 & \beta-2 & \alpha+8 & 22 & -12+\Delta & -84 & -56 & 0 \\
0 & \varepsilon & \delta & \gamma-1 & \beta-2 & \alpha+10 & 26 & -16+\Delta & -112 & -72 \\
0 & 0 & \varepsilon & \delta & \gamma-1 & \beta-2 & \alpha+12 & 30 & -20+\Delta & -144 \\
0 & 0 & 0 & \varepsilon & \delta & \gamma-1 & \beta-2 & \alpha+14 & 34 & -24+\Delta
\end{vmatrix}$$

(1.17)

$$\hat{N} = \begin{vmatrix} 1 & & & & & & \\ 2 & 1 & & & & & \\ 1 & 2 & 1 & & & & \\ 0 & 1 & 2 & 1 & & & \\ 0 & 0 & 1 & 2 & 1 & & \\ 0 & 0 & 0 & 1 & 2 & 1 & \\ 0 & 0 & 0 & 0 & 1 & 2 & 1 \end{vmatrix}$$

(1.18)

This is a somewhat different eigenvalue problem than usually encountered in spectroscopy in that the eigenvalue Λ appears not only on the principal diagonal but also on the first upper and lower diagonals. In addition, the banded matrix $\hat{M}$ is not symmetric.

Equation 1.16 is an example of the general eigenvalue problem which has been of recent interest to numerical analysis [5]. Fortunately our problem can be reduced to a simpler eigenvalue problem by noting that the banded matrix $\hat{N}$ is nonsingular (i.e., $\det \hat{N} \neq 0$), consequently its inverse N^{-1} exists. Premultiplying Eq. 1.16 by N^{-1} reduces it to

$$(\hat{N}^{-1}\hat{M} - \lambda\hat{I})\hat{C} = 0 \qquad (1.19)$$

which is a regular eigenvalue problem for a nonsymmetric matrix $\hat{A} \equiv \hat{N}^{-1}\hat{M}$. Numerical calculations will be carried out in the near future.

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1. J. Dunham, *Phys. Rev.* **41**, 1932, 721.

2. J. Kilpatrick, *J. Chem. Phys.* **30**, 1959, 801.

3. S. Chan and D. Stelman, *J. Mol. Spectrosc.* **49**, 1968, 1740.

4. C. Reid, *J. Mol. Spectrosc.* **36**, 1970, 183. Contains extensive references to the older literature on the quartic oscillator.

5. G. Peters and J. Wilkinson, *SIAM J. Numer. Anal.* **7**, 1970, 479.

2. MASS-DEPENDENT CONTRIBUTION TO THE POTENTIAL ENERGY IN THE WATSON MOLECULAR VIBRATION-ROTATION HAMILTONIAN

Among the many contributions made by Watson [1] in his important paper on the Darling-Dennison-Wilson Hamiltonian, Watson showed that the effective reciprocal inertia tensor $\mu_{\alpha\beta}$ (α β = 1,2,3) can be expanded as a Taylor series in the normal coordinates. The use of matrix notation for $\mu_{\alpha\beta}$ as a 3 × 3 matrix $\hat{\mu}$ enables the expansion to be cast into succinct form. The $\hat{\mu}$ matrix has the form

$$\hat{\mu} = (\hat{I}_0)^{-\frac{1}{2}} (\hat{E} + \tfrac{1}{2} \hat{b})^{-2} (\hat{I}_0)^{-\frac{1}{2}} \qquad (2.1)$$

where $\hat{E}$ is the unit matrix. Note that $\hat{E}$ and $\hat{b}$ commute, so we can use the binomial expansion of $(\hat{E} + 1/2\ \hat{b})^{-2}$; thus

$$\hat{\mu} = (\hat{I}_0)^{-\frac{1}{2}} \left[\hat{E} + \sum_{r=1}^{\infty} (r+1) (-\tfrac{1}{2})^r \hat{b}^r \right] (\hat{I}_0)^{-\frac{1}{2}} . \qquad (2.2)$$

The matrix $\hat{b}$ is also 3 × 3, consequently we can express any power of $\hat{b}$ greater than or equal to three in terms of the generalized Lucas polynomials of order three introduced by Barakat and Bauman [2] to handle just such problems.

The generalized Lucas polynomials of order three are defined by the recurrence relation [2]

$$U^{(3)}_{n+3}(\phi_1,\phi_2,\phi_3) = \phi_1 U^{(3)}_{n+2}(\phi_1,\phi_2,\phi_3) - \phi_2 U^{(3)}_{n+1}(\phi_1,\phi_2,\phi_3) + \phi_3 U^{(3)}_{n}(\phi_1,\phi_2,\phi_3) \qquad (2.3)$$

subject to the initial conditions

$$U_0^{(3)}(\phi_1,\phi_2,\phi_3) = 0 , \qquad U_2^{(3)}(\phi_1,\phi_2,\phi_3) = 1$$

$$U_1^{(3)}(\phi_1,\phi_2,\phi_3) = 0 , \qquad U_3^{(3)}(\phi_1,\phi_2,\phi_3) = \phi_1 . \tag{2.4}$$

The explicit solution of Eq. 2.3 subject to these initial conditions is

$$U_{n+2}^{(3)}(\phi_1,\phi_2,\phi_3) = \sum_{i,j,k} \frac{(i+j+k)!}{i!j!k!} (\phi_1)^i(-\phi_2)^j(\phi_3)^k \tag{2.5}$$

where $i + 2j + 3k = n$. The ϕ's are the symmetric functions formed by the traces of $\hat{b}$, $\hat{b}^2$, $\hat{b}^3$. The traces are invariant under a unitary transform and are thus independent of orientation. The ϕ's are related to the σ's (the traces of powers of $\hat{b}$, i.e., $\sigma_k \equiv \mathrm{tr}\hat{b}^k$) by

$$\phi_1 = \sigma_1$$

$$\phi_2 = \frac{1}{2}(\sigma_1^2 - \sigma_2)$$

$$\phi_3 = \frac{1}{6}(\sigma_1^3 - 3\sigma_1\sigma_2 + 2\sigma_3) . \tag{2.6}$$

Now, if we set

$$\hat{b} = \sum_k \hat{b}_k Q_k \tag{2.7}$$

where $\{Q_k\}$ are the normal coordinates, then

$$\hat{b}_k = \begin{vmatrix} b_k^{xx} & b_k^{xy} & b_k^{xz} \\ b_k^{yx} & b_k^{yy} & b_k^{yz} \\ b_k^{zx} & b_k^{zy} & b_k^{zz} \end{vmatrix} . \tag{2.8}$$

Straightforward calculations then yield

$$\text{tr } \hat{b} \equiv \sigma_1 = \sum_k g_k^{(1)} Q_k \tag{2.9}$$

$$\text{tr } \hat{b}^2 \equiv \sigma_2 = \sum_k \sum_\ell g_{k\ell}^{(2)} Q_k Q_\ell \tag{2.10}$$

$$\text{tr } \hat{b}^3 \equiv \sigma_3 = \sum_k \sum_\ell \sum_m g_{k\ell m}^{(3)} Q_k Q_\ell Q_m \tag{2.11}$$

where

$$g_k^{(1)} \equiv b_k^{xx} + b_k^{yy} + b_k^{zz} \tag{2.12}$$

$$g_{k\ell}^{(2)} \equiv b_k^{xx} b_\ell^{xx} + b_k^{yy} b_\ell^{yy} + b_k^{zz} b_\ell^{zz} + 2b_k^{xy} b_\ell^{yz} + 2b_k^{xz} b_\ell^{zx} + 2b_k^{yz} b_\ell^{zy} \tag{2.13}$$

$$\begin{aligned} g_{k\ell m}^{(3)} \equiv\ & b_k^{xx} b_\ell^{xx} b_m^{xx} + b_k^{yy} b_\ell^{yy} b_m^{yy} + b_k^{zz} b_\ell^{zz} b_m^{zz} \\ & + 3b_k^{xx} b_\ell^{xy} b_m^{yx} + 3b_k^{xx} b_\ell^{xz} b_m^{zx} + 3b_k^{yy} b_\ell^{yx} b_m^{xy} \\ & + 3b_k^{yy} b_\ell^{yz} b_m^{zy} + 3b_k^{zz} b_\ell^{zx} b_m^{xz} + 3b_k^{zz} b_\ell^{zy} b_m^{yz} \\ & + 3b_k^{xy} b_\ell^{yz} b_m^{zx} + 3b_k^{xz} b_\ell^{zy} b_m^{yx} \end{aligned} \tag{2.14}$$

Consequently, ϕ_1, ϕ_2, and ϕ_3 can be expressed directly in terms of the $\{Q_k\}$, the explicit formulae are

$$\sigma_1 \equiv \text{tr } \hat{b} = \sum_k h_k^{(1)} Q_k \tag{2.15}$$

$$\sigma_2 \equiv \text{tr } \hat{b}^2 = \sum_{k,\ell} h_{kk}^{(2)} Q_k Q_\ell \tag{2.16}$$

$$\sigma_3 \equiv \text{tr } \hat{b}^2 = \sum_{k,\ell,m} h_{k\ m}^{(3)} Q_k Q_\ell Q_m \tag{2.17}$$

with

$$h_k^{(1)} \equiv g_k^{(1)} \tag{2.18}$$

$$h_{k\ell}^{(2)} \equiv \frac{1}{2} g_k^{(1)} g_\ell^{(1)} - \frac{1}{2} g_{k\ell}^{(2)} \tag{2.19}$$

$$h_{k\ell m}^{(3)} \quad \frac{1}{6} g_k^{(1)} g_\ell^{(1)} g_m^{(1)} - \frac{1}{2} g_k^{(1)} g_{\ell m}^{(2)} + \frac{1}{3} g_{k\ell m}^{(3)} . \tag{2.20}$$

Note that σ_1 is linearly dependent on $\{Q_k\}$, σ_2 is a quadratic function of $\{Q_k\}$, while σ_3 is a cubic function of $\{Q_k\}$. All higher σ's can be written in terms of σ_1, σ_2, and σ_3. In fact, we can prove

$$\sigma_k = U_k^{(3)} \sigma_2 + [U_{k+1}^{(3)} - \phi_1 U_k^{(3)}] \sigma_1 + 3\phi_1 U_{k-1}^{(3)} \tag{2.21}$$

for $k \geq 3$.

Barakat and Bauman [2] have shown that any positive power of $\hat{b}$ greater than or equal to three can be expressed as

$$\hat{b}^r = U_r^{(3)}\hat{b}^2 + [U_{r+1}^{(3)} - \phi_1 U_r^{(3)}]\hat{b} + \phi_3 U_{r-1}^{(3)}\hat{E} \ . \qquad (2.22)$$

This equation is the key to the subsequent analysis. Let us return to Eq. 2.2 and employ Eq. 2.22 in the right hand side, the result is

$$\hat{\mu} = (\hat{I}_0)^{-\frac{1}{2}} \left\{ \hat{E} - \hat{b} + \frac{3}{8}\hat{b}^2 + \sum_{r=3}^{\infty} (r+1)\left(-\frac{1}{2}\right)^r U_r^{(3)}\hat{b}^2 \right.$$

$$+ \sum_{r=3}^{\infty} (r+1)\left(-\frac{1}{2}\right)^r \left[U_{r+1}^{(3)} - \phi_1 U_r^{(3)}\right]\hat{b}$$

$$\left. + \sum_{r=3}^{\infty} (r+1)\left(-\frac{1}{2}\right)^r \phi_3 U_{r-1}^{(3)}\hat{E} \right\} (\hat{I}_0)^{-\frac{1}{2}} \qquad (2.23)$$

or

$$\hat{\mu} = (\hat{I}_0)^{-1} - (\hat{I}_0)^{-\frac{1}{2}}\hat{b}(\hat{I}_0)^{-\frac{1}{2}} + \frac{3}{4}(\hat{I}_0)^{-\frac{1}{2}}\hat{b}^2(\hat{I}_0)^{-\frac{1}{2}} + \sum_{r=3}^{\infty} (r+1)\left(-\frac{1}{2}\right)^r$$

$$\cdot U_r^{(3)}(\hat{I}_0)^{-\frac{1}{2}}\hat{b}^2(\hat{I}_0)^{-\frac{1}{2}} + \sum_{r=3}^{\infty} (r+1)\left(-\frac{1}{2}\right)^r \left[U_{r+1}^{(3)} - \phi_1 U_r^{(3)}\right]$$

$$\cdot (\hat{I}_0)^{-\frac{1}{2}}\hat{b}(\hat{I}_0)^{-\frac{1}{2}} + \sum_{r=3}^{\infty} (r+1)\left(-\frac{1}{2}\right)^r \phi_3 U_{r-1}^{(3)} (\hat{I}_0)^{-1} \ . \qquad (2.24)$$

Actually we really want to work with the $\hat{a}$-matrices given in Watson [1]

$$\hat{b} = (\hat{I}_0)^{-\frac{1}{2}}\hat{a}(\hat{I}_0)^{-\frac{1}{2}} . \tag{2.25}$$

Now,

$$(\hat{I}_0)^{-\frac{1}{2}}\hat{b}(\hat{I}_0)^{-\frac{1}{2}} = (\hat{I}_0)^{-1}\hat{a}(\hat{I}_0)^{-1} . \tag{2.26}$$

We can also show that

$$(\hat{I}_0)^{-\frac{1}{2}}\hat{b}^2(\hat{I}_0)^{-\frac{1}{2}} = (\hat{I}_0)^{-1}\hat{a}(\hat{I}_0)^{-1}\hat{a}(\hat{I}_0)^{-1} . \tag{2.27}$$

Upon employing the expressions in Eq. 2.24, we can express $\hat{\mu}$ entirely in terms of the $\hat{a}$. The final result is

$$\hat{\mu} = A(\hat{I}_0)^{-1} + B(\hat{I}_0)^{-1}\hat{a}(\hat{I}_0)^{-1} + C(\hat{I}_0)^{-1}\hat{a}(\hat{I}_0)^{-1}\hat{a}(\hat{I}_0)^{-1} \tag{2.28}$$

where

$$A \equiv 1 + \sum_{r=3}^{\infty} (r+1)\left(-\frac{1}{2}\right)^r \phi_3 U_{r-1}^{(3)}(\phi_1,\phi_2,\phi_3) \tag{2.29}$$

$$B \equiv -1 + \sum_{r=3}^{\infty} (r+1)\left(-\frac{1}{2}\right)^r [U_{r+1}^{(3)}(\phi_1,\phi_2,\phi_3) - \phi_1 U_r^{(3)}(\phi_1,\phi_2,\phi_3)] \tag{2.30}$$

$$C \equiv \frac{3}{4} + \sum_{r=3}^{\infty} (r+1)\left(-\frac{1}{2}\right)^r U_r^{(3)}(\phi_1,\phi_2,\phi_3) . \tag{2.31}$$

Although Eq. 2.28 is the desired result, we still have to express A, B, and C in terms of $\{Q_k\}$. This is easily accomplished, albeit tedious. In C, we encounter $U_r^{(3)}$ alone. Upon employing

the explicit expressions for $U_r^{(3)}$ listed in Barakat and Bauman, we can prove that

$$U_r^{(3)} = \sum_{k_1} \sum_{k_2} \cdots \sum_{k_r} G^{(r-2)}_{k_1 k_2 \cdots k_r} Q_{k_1} Q_{k_2} \cdots Q_{k_r} \tag{2.32}$$

with

$$G^{(1)}_{k_1} = g^{(1)}_{k_1} \tag{2.33}$$

$$G^{(2)}_{k_1 k_2} \equiv \frac{1}{2} g^{(1)}_{k_1} g^{(1)}_{k_2} + \frac{1}{2} g^{(2)}_{k_1 k_2} \tag{2.34}$$

$$G^{(3)}_{k_1 k_2 k_3} \equiv \frac{1}{3} g^{(3)}_{k_1 k_2 k_3} + \frac{1}{6} g^{(1)}_{k_1} g^{(1)}_{k_2} g^{(1)}_{k_3} + \frac{1}{2} g^{(1)}_{k_1} g^{(2)}_{k_2 k_3} \tag{2.35}$$

$$G^{(4)}_{k_1 k_2 k_3 k_4} \equiv \frac{1}{12} g^{(1)}_{k_1} g^{(1)}_{k_2} g^{(1)}_{k_3} g^{(1)}_{k_4} + \frac{2}{3} g^{(1)}_{k_1} g^{(3)}_{k_2 k_3 k_4} + \frac{1}{4} g^{(2)}_{k_1 k_2} g^{(2)}_{k_3 k_4} \tag{2.36}$$

$$G^{(5)}_{k_1 \cdots k_5} \equiv \frac{1}{12} g^{(1)}_{k_1} g^{(1)}_{k_2} g^{(1)}_{k_3} g^{(1)}_{k_4} g^{(1)}_{k_5} + \frac{1}{3} g^{(2)}_{k_1 k_2} g^{(3)}_{k_3 k_4 k_5} + \frac{1}{4} g^{(1)}_{k_1} g^{(1)}_{k_2} g^{(3)}_{k_3 k_4 k_5} - 2 g^{(1)}_{k_1} g^{(1)}_{k_2} g^{(1)}_{k_3} g^{(2)}_{k_4 k_5} \tag{2.37}$$

$$G^{(6)}_{k_1 \cdots k_6} \equiv \frac{1}{2} g^{(1)}_{k_1} g^{(1)}_{k_2} g^{(1)}_{k_3} g^{(1)}_{k_4} g^{(1)}_{k_5} g^{(1)}_{k_6} - \frac{4}{3} g^{(1)}_{k_1} g^{(1)}_{k_2} g^{(1)}_{k_3} g^{(1)}_{k_4} g^{(2)}_{k_5 k_6} + \frac{1}{3} g^{(1)}_{k_1} g^{(1)}_{k_2} g^{(1)}_{k_3} g^{(2)}_{k_4 k_5 k_6} + g^{(1)}_{k_1} g^{(2)}_{k_2 k_3} g^{(3)}_{k_4 k_5 k_6} . \tag{2.38}$$

The method is ideally suited to automatic evaluation on a

computer and there is no need to carry out higher order explicit results by hand.

The series in A contains the function

$$W_{r+2}^{(3)} \equiv Q_3 U_{r-1}^{(3)} , \qquad r = 3,4,\cdots \tag{2.39}$$

while the series in B contains

$$V_{r+1}^{(3)} \equiv U_{r+1}^{(3)} - \phi_1 U_r^{(3)} , \qquad r = 3,4,\cdots \tag{2.40}$$

The first few members of both sets have been worked out explicitly and are

$$W_5^{(3)} = \sum_{k_1 k_2 k_3} h_{k_1 k_2 k_3}^{(3)} Q_{k_1} Q_{k_2} Q_{k_3} \tag{2.41}$$

$$W_6^{(3)} = \sum_{k_1 \cdots k_4} h_{k_1 k_2 k_3}^{(3)} g_{k_4}^{(1)} Q_{k_1} \cdots Q_{k_4} \tag{2.42}$$

$$W_7^{(3)} = \sum_{k_1 \cdots k_5} h_{k_1 k_2 k_3}^{(3)} G_{k_4 k_5}^{(3)} Q_{k_1} \cdots Q_{k_6} \tag{2.43}$$

$$W_8^{(3)} = \sum_{k_1 \cdots k_6} h_{k_1 k_2 k_3}^{(3)} G_{k_4 k_5 k_6}^{(3)} Q_{k_1} \cdots Q_{k_6} \tag{2.44}$$

for the $W^{(3)}$ functions. The $V^{(3)}$ functions are

$$V_4^{(3)} = \sum_{k_1 k_2} \left[G_{k_1 k_2}^{(2)} - g_{k_1}^{(1)} g_{k_2}^{(1)} \right] Q_{k_1} Q_{k_2} \tag{2.45}$$

$$V_5^{(3)} = \sum_{k_1 k_2 k_3} \left[G^{(3)}_{k_1 k_2 k_3} - g^{(1)}_{k_1} G^{(2)}_{k_2 k_3} \right] Q_{k_1} Q_{k_2} Q_{k_3} \tag{2.46}$$

$$V_6^{(3)} = \sum_{k_1 \cdots k_4} \left[G^{(4)}_{k_1 k_2 k_3 k_4} - g^{(1)}_{k_1} G^{(3)}_{k_2 k_3 k_4} \right] Q_{k_1} \cdots Q_{k_4} \tag{2.47}$$

$$V_7^{(3)} = \sum_{k_1 - k_5} \left[G^{(5)}_{k_1 k_2 k_3 k_4 k_5} - g^{(1)}_{k_1} G^{(4)}_{k_2 k_3 k_4 k_5} \right] Q_{k_1} \cdots Q_{k_5} \tag{2.48}$$

$$V_8^{(3)} = \sum_{k_1 - k_6} \left[G^{(6)}_{k_1 - k_6} - g^{(1)}_{k_1} G^{(5)}_{k_2 - k_6} \right] Q_{k_1} \cdots Q_{k_6} . \tag{2.49}$$

To summarize, the explicit forms of A, B, C are:

$$A = \left[1 - \frac{1}{2} W_5^{(3)} + \frac{5}{16} W_6^{(3)} - \frac{3}{16} W_7^{(3)} + \frac{7}{64} W_8^{(3)} \right] \tag{2.50}$$

$$B = \left[1 + \frac{1}{2} V_4^{(3)} - \frac{5}{16} V_5^{(3)} + \frac{3}{16} V_6^{(3)} - \frac{7}{64} V_7^{(3)} + \frac{9}{256} V_8^{(3)} \right] \tag{2.51}$$

$$C = \left[\frac{3}{4} - \frac{1}{2} U_3^{(3)} + \frac{5}{16} U_4^{(3)} - \frac{3}{16} U_5^{(3)} + \frac{7}{64} U_6^{(3)} - \frac{1}{16} U_7^{(3)} + \frac{9}{256} U_8^{(3)} \right] \tag{2.52}$$

to sixth-order in the Q_k.

These results are essentially equivalent to those obtained by Rothman [3] using an iterative scheme. Dr. Rothman kindly lent me some numerical results obtained via his approach, the present more explicit method yielded the same numerical results.

NOTE ON OTHER SCHEMES

The author had originally hoped that the method of matrix Padé approximants [4] could be utilized directly to handle Eq. 2.1. Unfortunately this approach is almost useless because one cannot explicitly calculate anything except the first matrix Padé approximant. In view of this fact, we omit any discussion of the method and of our fruitless manipulations directed toward this end.

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3. NOTE ON A CHEBYSCHEV OPERATOR EXPANSION OF THE van VLECK TRANSFORMATION

The van Vleck transformation has been applied to the problem of vibration-rotation interaction of polyatomic (and particularly triatomic) molecules by various investigators, for one of the more successful attempts see Rothman and Clough [*1*].

I have made an attempt to seek a different type of expansion of the van Vleck transformation that would converge more rapidly than the usual power series procedure and yet hopefully retain the versatile attributes of the power series. A method that appeared to have both properties is a Chebyschev expansion extended to operators. It is well known among numerical analysts that Chebyschev expansions are more rapidly convergent than the corresponding power series [*2*].

The van Vleck transformation is

$$\hat{H}' = e^{i\lambda\hat{S}}\,\hat{H}\,e^{-i\lambda\hat{S}} \tag{3.1}$$

where the operator $\hat{S}$ is hermitian and λ is an expansion parameter whose value lies between zero and unity. For our purposes, it is more convenient to deal with the "real" and "imaginary" parts of the right hand side of Eq. 3.1; thus

$$\hat{R} \equiv (\cos\lambda\hat{S})\hat{H}(\cos\lambda\hat{S}) + (\sin\lambda\hat{S})\hat{H}(\sin\lambda\hat{S}) \tag{3.2}$$

$$\hat{I} \equiv (\sin\lambda\hat{S})\hat{H}(\cos\lambda\hat{S}) - (\cos\lambda\hat{S})\hat{H}(\sin\lambda\hat{S})\ . \tag{3.3}$$

The basic idea is to utilize the expansions

$$\cos\lambda\hat{S} = J_0(\lambda) + 2\sum_{n=1}^{\infty}(-1)^n J_{2n}(\lambda)T_{2n}(\hat{S})$$

$$\sin\lambda\hat{S} = 2\sum_{n=1}^{\infty}(-1)^n J_{2n+1}(\lambda)T_{2n+1}(\hat{S})$$

where $T_n(\hat{S})$ is the Chebyschev polynomial of degree n in the operator $\hat{S}$. In order that this method work it is manditory that the norm of $\hat{S}$ be less than or equal to unity, which is a severe restriction.

Although these expressions converge rapidly they cannot be utilized in their present form since they must be rearranged in power of λ in order to be useful. This requires that we write out the power series expansions of $J_n(\lambda)$ and collect equal powers of λ.

Unfortunately, when this extremely tedious procedure was carried out, the resultant expressions are so involved that any attempt to actually perform the van Vleck transformation was frustrated by the cumbersome formulae. This possible approach does not offer any advantages over the usual power series approach to the van Vleck transformation.

REFERENCES

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